COPOLYMERS WITH BUTADIENE OF THE *CIS*- AND *TRANS*- 1-CYANO-1,3-BUTADIENES

BY

KEITH CHADWICK MURDOCK

B.A., University of Utah, 1948
M.A., University of Utah, 1950

R. UNIV. BIBLIOTHEEK LEIDEN

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1953

URBANA, ILLINOIS

1953

COPOLYMERS WITH BUTADIENE OF THE *CIS*- AND *TRANS*- 1-CYANO-1,3-BUTADIENES

BY

KEITH CHADWICK MURDOCK

B.A., University of Utah, 1948
M.A., University of Utah, 1950

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1953

URBANA, ILLINOIS

1953

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. Harold R. Snyder and Dr. Carl S. Marvel who jointly suggested and directed this investigation. Their encouragement and advice have been sincerely appreciated.

The author is also deeply grateful to the late Dr. Elliot R. Alexander for his enthusiastic and stimulating direction of an earlier investigation which was discontinued after his untimely death. Thanks are due to the University of Illinois for a teaching assistantship, a fellowship, and a research assistantship.

The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program. The author is indebted to Mr. W. K. Taft of the University of Akron for his evaluations of the elastomers prepared.

COPOLYMERS WITH BUTADIENE OF THE *CIS-* AND *TRANS-* 1-CYANO-1,3-BUTADIENES

Introduction

In the search for an elastomer which is not only resistant to the solvent action of various fuels and oils, but also maintains its rubber-like properties at low temperatures, a number of vinyl compounds having various polar substituents have been copolymerized with butadiene.

Copolymers of butadiene with 1-cyano-1,3-butadiene have shown good oil resistance and seemed to show promising low temperature properties, particularly when the *cis-trans*-1-cyano-butadiene used was rich in the difficultly accessible *trans* isomer.[1] The object of the present investigation, therefore, was to isolate a quantity of the pure *trans* isomer and to prepare and evaluate copolymers of it with butadiene.

Discussion

A mixture of the *cis-* and *trans*-1-cyano-1,3-butadienes was prepared *via* the pyrolysis of crotonaldehyde cyanohydrin benzoate.[2] The isolation of a quantity of the pure *trans* cyanodiene, previously blocked[1] because of the great ease with which the diene undergoes a Diels-Alder dimerization, was accomplished by the development of a low-temperature fractional distillation technique.

Copolymerization of butadiene with either the *cis-* or *trans*-1-cyano-1,3-butadiene was best conducted in an emulsion system at 50°C. employing azo-*bis*-isobutyronitrile as an initiator of polymerization. The course of the polymerization was followed by quantitative rate and composition studies. Contrary to expectation it was found that the *cis* cyanodiene underwent polymerization more than twice as rapidly as the *trans* isomer. However, with various *cis-trans* mixtures, at any given per cent conversion the amount of cyanodiene

incorporated into the copolymer was independent of the *cis-trans* ratio in the comonomer charge. Accordingly, it was thought that there was no actual difference in the reactivities of the *cis* and *trans* isomers, but that inhibitory by-products were engendered by the *trans* isomer during its copolymerization.

The inhibition was thought to be due to the generation of both the dimer of the *trans* cyanodiene, *cis*-1-cyano-2-(*trans*-2-cyanovinyl)-5-cyclohexene,[3] and the similar Diels-Alder-type adduct of the *trans* cyanodiene with butadiene, partially characterized[4] as a 1-cyano-2-vinylcyclohexene. Compounds with doubly activated hydrogen atoms such as 1,4-pentadiene and cyclopentadiene have been shown to be powerful inhibitors of polymerization.[5] The cyanodiene dimer (and probably the butadiene adduct) has a hydrogen atom which is not only allylic, but is *alpha* to a cyano group. In a concentration of one-fourth of one per cent by weight of the monomer charge the cyanodiene dimer was found to inhibit markedly the polymerization of butadiene.

Thus it was concluded that in their copolymerization with butadiene the *cis*- and *trans*-1-cyano-1,3-butadienes exhibit identical monomer reactivity ratios. The values for these ratios as determined[6] by Wall and co-workers for the *cis* isomer, $r_1 = 1.7$ and $r_2 = 0.0$, accordingly would be applicable to either of the pure isomers or to any of their mixtures.

As would be expected from the reactivities of the isomeric cyanodienes and the probable loss of their geometrical differences after their addition to a growing polymer chain, their copolymers with butadiene were practically identical. Infrared studies indicated identity in the amounts of *cis*-1,4-, *trans*-1,4, and 1,2-addition of the copolymer chain units. A variety of elastomer evaluation procedures also showed no significant differences between the two copolymers. They exhibited excellent oil resistance and showed little tendency to crystallize at low temperatures, but they did become stiff and sluggish even at considerably higher temperatures.

BIBLIOGRAPHY

1. Office of Rubber Reserve, private communications.

2. H. R. Snyder, J. M. Stewart and R. L. Myers, J. Am. Chem. Soc., **71**, 1055 (1949).

3. J. L. Charlish and W. H. Davies, J. Chem. Soc., 1385 (1950).

4. H. R. Snyder and G. I. Poos, J. Am. Chem. Soc., **71**, 1057 (1949).

5. R. L. Frank, C. E. Adams, J. R. Blegen, R. Deanin, and P. V. Smith, Ind. Eng. Chem., **39**, 887 (1947) ; R. L. Frank, J. R. Blegen, G. E. Inskeep, and P. V. Smith, *ibid.*, **39**, 893 (1947).

6. F. T. Wall, R. W. Powers, G. D. Sands and G. S. Stent, J. Am. Chem. Soc., **70**, 1031 (1948).

VITA

The author was born in Garfield, Utah, on February 5, 1928. After attending public schools in Salt Lake City, Utah, Westfield, New Jersey, Fairbanks, Alaska, and Palo Alto, California, he was graduated from Carbon High School, Price, Utah, in 1944. He enrolled in the University of Utah in September, 1944, where he received the degrees of Bachelor and Master of Arts in June, 1948, and June, 1950, respectively. In March of 1950 he entered the Graduate College of the University of Illinois where he held a half-time teaching assistantship from September, 1950, to June, 1951. During the summer of 1951 he was employed in the Pharmaceutical Research Section of the American Cyanamid Company, Calco Chemical Division, Bound Brook, New Jersey. He held a University of Illinois Fellowship from September, 1951, until February, 1952, and a University Research Assistantship in connection with the Government Synthetic Rubber Program from February, 1952, to February, 1953.